Conversion Process of Molten Fly Ash into Functional Materials using Waste Plastics

Takaaki WAJIMA*

*Department of Urban Environment Systems, Graduate School of Engineering, Chiba University, Chiba 263-8522, Japan
E-mail : wajima@tu.chiba-u.ac.jp

A new two-step process, chlorination reduction of molten fly ash with waste plastics (PVC) to separate harmful substances, such as Na, K, Cl, Zn and Pb, from the ash, and transformation from the ash into functional materials by hydrothermal treatment with sodium hydroxide, was attempted. The ash was mixed with PVC (1 : 1), and then the mixture was heated at 1000°C in nitrogen gas. After heating, the residue was heated again at 1000°C in air to obtain the treated ash. Although raw ash contains harmful substances such as Na, K, Cl, Zn and Pb, treated ash has lower contents of these substances than raw ash. Mineral phases in treated ash are mainly gehlenite, due to the disappearance of sodium chloride and potassium chloride in raw ash by two-step treatment with PVC. While a large amount of harmful ions, (Na^+ , K^+ , Cl^- , Zn^{2+} and Pb^{2+}) were eluted, the elution of Na^+ and K^+ from treated ash was not observed, and those of Cl^- , Zn^{2+} and Pb^{2+} decreased. Raw ash or treated ash was treated with 2 M NaOH solution at 180°C for 20 h to obtain functional materials. From both ashes, tobermorite 11 Å and hydroxyapatite can be synthesized.

Key Words : Waste plastics, Molten fly ash, Heating, Alkali treatment, Tobermorite 11 Å, Hydroxyapatite

1 INTRODUCTION

Waste incineration ash produced by burning waste generated in our daily lives is becoming a severe social problem. Recently, municipal solid waste (MSW) is treated using gasifying and melting furnace, and a large part of the molten fly ash, which is handled as a specially-controlled waste in the same manner as incineration fly ash (fly ash from stoker-type incinerators), is generated. In Japan, more than 0.1 million tons of MSW molten fly ash is estimated to be discharged every year as a result of an increasing number of MSW melting plants [1]. This molten fly ash generally contains harmful substances, especially heavy metals such as lead, zinc, and copper, and is disposed of by landfill burial after stabilization treatment by methods designated by the national government, such as chelate treatment or cement fixation. Furthermore, a shortage of landfill disposal sites has become a major social problem. The establishment of a technology which separates harmful substances such as lead, zinc, etc. in fly ash as completely as possible, and enables recycling of the residue has been desired.

In addition, the content of heavy metals is usually higher than that of their respective metal ores [2]. Given this, it seems to be of great importance to develop effective separation technologies for removal and recovery of heavy metals from molten fly ash. Recently, wet processes such as acid extraction [3-5], electrodialytic separation [6], and solvent extraction [7] have been proposed for metal recovery from molten fly ash, and it was reported that these methods can be used to recover heavy metals in a highly concentrated form. Separation techniques based on dry processes such as reduced volatilization and chloride-induced volatilization

has been recently proposed. In the case of reduced volatilization, separation of heavy metals from molten fly ash has been studied [1]. As a result, zinc and lead recovery levels from molten fly ash as high as 90% were achieved at 1573 K, and in addition, 99% of the dioxin content was decomposed. Furthermore, it was reported that 95% of lead and zinc were volatilized from molten fly ash in the presence of reducing agents, carbon and polyvinyl chloride (PVC) [8-12]. Moreover, to reduce energy consumption, volatilization and separation of heavy metals by chloride-induced volatilization has been studied by several researchers using CaCl_2 , etc. [13-16]. In general, the inorganic chlorides, NaCl, KCl, and CaCl_2 are present in molten fly ash, and these inorganic chlorides are supposed to function as chlorinating agents, and the volatilization of heavy metals was found to increase with addition of inorganic chlorides and the increase became higher in order $\text{CaCl}_2 > \text{NaCl} > \text{KCl}$ [17].

This research was based on the idea that target metals of the ash can be recovered as chlorides by volatilization using waste polyvinyl chloride (PVC) as the source of chlorine and reductant. PVC is the second most important polymer worldwide and a large-scale chemical product. Thanks to its excellent cost/performance ratio and outstanding chemical and environmental resistance, it is today mainly used for long-life applications. However, plastic wastes have an immense impact on the environment because plastics are non-biodegradability and take a long time to break down when they are landfill [18]. Therefore, new ways to use waste plastics are desired. PVC is composed of about 57% chlorine and about 43% hydrocarbon. It begins emitting hydrogen chloride gas by pyrolysis under 300°C and remains hydrocarbon. Hydrogen chloride gas may pose a problem during the incineration of waste, but it can be used as a provider of chlorine. Moreover, the residual

hydrocarbon of PVC can be used as a reductant.

After the removal of harmful substances, the residual ash, which is desired for recycling, are produced. Though use of waste ash as a raw material for cement synthesis has been attempted, the technology faces problems such as cost and quality. One of the recycling ways of the ash is to convert the ash into useful material. Many researchers have reported the conversion of incineration fly ashes, noticing that the main components of the ash were SiO_2 , Al_2O_3 and CaO , into materials such as zeolite, tobermorite and hydrogrossular, to be used for environmental purification [19-25]. Therefore, it is considered that material conversion from the ash without harmful substances into functional materials for environmental application is favorable.

In this study, a novel two-step treatment process using two kinds of waste, molten fly ash and waste PVC, was attempted to remove heavy metals from the ash as metal chloride for recovery as metal resources and also to convert the residual ash into functional materials for environmental applications. For feasibility study, firstly, the characteristics of the residue after heating of the mixture of the ash and PVC were investigated, and secondly material conversions of raw ash and the residual ash were undertaken under identical conditions, using NaOH as the activation reagent, and the products were compared. As a result, a new treatment technology which enables advanced detoxification of molten fly ash and effective utilization of the residue was suggested.

2 EXPERIMENTAL

Molten fly ash, which was discharged from one of the melting furnace plants in Japan, was used in this study, and PVC powder was purchased from Wako Pure Industries, Ltd., Japan. Morphologies of these samples were shown in Figure 1. Experimental procedure is shown in Figure 2. The raw ash was

Figure 1 SEM photographs of (a) molten fly ash and (b) PVC.

Figure 2 Flow chart of this experiments.

heated at 1000°C in air and N_2 atmosphere with or without PVC to separate harmful elements such as Na, K, Cl, Zn and Pb from the ash. Then, the heat-treated ash was treated with alkali solution to convert into functional materials.

2.1 Reduction of harmful contents

Air-heating and N_2 -heating were attempted to apply for reduction of harmful content in molten fly ash.

Air-heating was performed as follows. Two g of molten fly ash was put in an alumina crucible, and set in an electric furnace. The furnace heated the crucible with increasing temperature to 1000°C for 2 h, and then heated at 1000°C for 3 h. After heating, the crucible was cooled to room temperature to obtain the ash treated with air-heating.

N_2 -heating was performed in a horizontal reactor as follows. Two g of molten fly ash was put in a ceramic board, and installed in a transparent quartz tube of 0.45 m inside diameter and 1 m in length. Before heating, N_2 gas was injected into the tube for 30 min at a rate of 1.0 L/min to replace the air in the tube. The electric tube furnace heated the ash in the reactor with increasing temperature to 1000°C for 1.5 h, and then the ash was heated at 1000°C for 3 h, with a continuous flow of N_2 gas at a rate of 1.0 L/min. After heating, the product was cooled to room temperature with a steady N_2 gas flow (1.0 L/min) in the tube to obtain the ash treated with N_2 -heating.

In this experiment, four heating treatment processes with different combinations of air-heating for removal of organic carbonaceous content, and N_2 -heating for reduction of metal oxides were carried out (Figure 3). While molten fly ash was used directly for heating in process-1 and pocess-2, the mixture of the ash and PVC, which 1 g of the ash was mixed with 1 g of PVC in a mortar, was used in process-3 and process-4. Process-1 and process-2 involved obtaining the ashes treated with air-heating (Ash-1) and N_2 -heating (Ash-2), respectively. Process-3 involved obtaining the ash with N_2 -heating from the mixture of molten fly ash and PVC (Ash-3), and process-4 involved obtaining the ash with air-heating from ash-3 (Ash-4). The mineralogical and chemical compositions of obtained ashes were analyzed, and reduction of harmful elements in the ash was determined by elution test.

2.2 Elution test

Elution tests were carried out on raw ash and treated ashes. 0.1 g of the ash was added to 10 mL of distilled water in 50 mL of tube, and then the tube was shaken for 12 hour with reciprocal shaker. After shaking at room temperature, the suspension was centrifuged to collect the supernatant. The concentrations of Na^+ , K^+ , Cl^- , Zn^{2+} ,

Figure 3 Flow chart of the four processes.

Table 1 Chemical compositions of raw ash, the products from raw ash and Ash-4.

	Chemical composition (wt. %)												
	Na ₂ O	K ₂ O	Cl	ZnO	PbO	CuO	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃
Raw ash	14.9	8.6	11.0	11.7	1.8	0.6	11.9	9.0	16.0	1.9	1.4	5.6	5.4
Product from raw ash	N.D.	1.0	0.4	8.5	1.2	0.9	23.4	11.1	35.0	4.6	2.4	10.4	1.3
Product from Ash-4	N.D.	0.6	0.7	1.9	N.D.	0.9	26.3	12.6	37.5	4.4	2.7	11.6	0.8

N. D.: Not detected

Pb²⁺ and Cu²⁺ in the supernatant were measured, and the elution amounts of each elements from the ashes (q_M) were calculated as follows;

$$q_M = C \cdot V / w \quad M: \text{Na}^+, \text{K}^+, \text{Cl}^-, \text{Zn}^{2+}, \text{Pb}^{2+}, \text{Cu}^{2+} \quad (1)$$

where C is the concentration of each elements in the supernatant after elution test (mg/L), V is the volume of aqueous solution (L), and w the weight of the ash added to distilled water (g).

2.3 Material conversion

Material conversion was performed in 50 mL Teflon-lined autoclave. 0.2 g of the ash was added into 5 mL of 2 M NaOH solution in autoclave, and then heated at 180°C for 20 h in electric furnace. After reaction, the solid product was separated from the solution by filtration, washed with distilled water and dried at 60°C overnight in a drying oven. The mineralogical phases of obtained products were determined.

2.4 Analysis

The mineralogical compositions of samples were determined by X-ray diffraction (Ultima, Rigaku, Japan), and chemical compositions of samples for typical main elements of incinerated fly ash as oxides, Na₂O, K₂O, Cl, ZnO, PbO, CuO, SiO₂, Al₂O₃, CaO, MgO, Fe₂O₃, P₂O₅ and SO₃, were analyzed by X-ray fluorescence (Primini, Rigaku, Japan). The morphologies of the samples were observed with scanning electron microscope (JSM890, JEOL, Japan). The concentrations of Na⁺, K⁺, Zn²⁺, Pb²⁺ and Cu²⁺ in the solution were analyzed by inductively-coupled plasma spectrometry (SPS4000, SEIKO, Japan), and Cl⁻ concentration in the solution was measured by ion chromatograph (ICS-3000, Dionex, Japan).

3 RESULTS AND DISCUSSION

3.1 Characterization of heat-treated ashes

Table 1 and figure 4 show the chemical and mineralogical compositions of molten fly ash and heat-treated ashes, respectively. Molten fly ash contains high amount of sodium, potassium and chloride as NaCl and KCl, and heavy metals, lead, zinc and copper, in the oxide forms PbO, ZnO, and CuO. Therefore, in this research, we classified Na, K, Cl, Zn, Pb and Cu as the harmful substances for elution test, and others are residual elements in the ash to synthesize functional materials. For mineral phases of heat-treated ashes, gehlenite (Ca₂Al₂SiO₇) mainly contains, and NaCl and KCl became minor, due to the melting point of NaCl (318°C) and KCl (776°C). The peaks of gehlenite is the highest and other peaks, which indicates harmful substances, are the lowest for Ash-4 via N₂-heating and air-heating with PVC.

Table 2 shows the solubility of harmful elements from raw ash and heated ashes. The solubility of Na⁺, K⁺ and Cl⁻ in Ash-1 is lower than those in raw ash, and those in Ash-2, Ash-3 and Ash-4 are far lower than those in raw ash. These results suggested that heat-treatment can reduce the elution of Na⁺, K⁺ and Cl⁻ from the ash, and the reduction of these elements elution using N₂-heating

Figure 4 shows XRD patterns of (a) raw ash, (b) Ash-1, (c) Ash-2, (d) Ash-3 and (e) Ash-4.

Table 2 Solubility of harmful elements from raw ash and heat-treated ashes.

	Solubility (mg/g)					
	Na ⁺	K ⁺	Cl ⁻	Zn ²⁺	Pb ²⁺	Cu ²⁺
Molten fly ash	54.0	62.7	210.7	0.26	0.24	0.17
Ash-1	32.3	13.0	146.5	0.21	0.33	0.17
Ash-2	27.6	11.3	17.9	0.31	0.27	0.17
Ash-3	0.6	0.6	43.9	0.13	N.D.	0.17
Ash-4	N.D.	N.D.	10.8	N.D.	N.D.	0.17

N. D. : Not Detected

is higher than that using air-heating. In addition, the reduction of Na⁺ and K⁺ using N₂-heating with PVC is higher than those without PVC. For heavy metals, the elution of Zn²⁺ and Pb²⁺ can be reduced by heat-treatment with PVC, while those are almost same by heat-treatment without PVC. Regardless of heat-treatment, the elution of Cu²⁺ is unchanged, which is consistent with the CuO remain in the ash shown in Figure 4. In Ash-1 and Ash-2, NaCl and KCl were melted, but metal chlorides to be vaporized were not formed because metal oxides in the ash are difficult to react with chloride [12]. On the other hands, in Ash-3 and Ash-4, metal oxides were reduced by PVC via N₂-heating, and sufficient amount of chloride from NaCl, KCl and PVC was reacted with reduced metals to form

Table 3 Chemical compositions for raw ash and heat-treated ashes

	Chemical composition (wt. %)						
	SiO ₂	Al ₂ O ₃	CaO	MgO	Fe ₂ O ₃	P ₂ O ₅	SO ₃
Molten fly ash	23.2	17.6	31.2	3.8	2.8	10.9	10.5
Ash-1	22.8	16.6	33.0	4.2	2.6	10.5	10.3
Ash-2	24.2	16.7	32.8	3.9	2.7	10.7	9.0
Ash-3	21.3	17.2	35.1	3.4	3.0	12.6	7.4
Ash-4	24.8	17.4	34.5	4.6	2.5	11.1	5.1

N. D. : Not Detected

metal chloride [8-10]. For Ash-4, residual carbon and chloride after N₂-heating were reacted with residual metals via air-heating. In addition, oxides of zinc and lead can be removed easier than that of copper in the ash by chlorination and carbo-chlorination, due to the difference of energy to form metal or metal chloride [12]. Therefore, removal of each metals in the ash are different, and CuO remained in the heat-treated ash on this experimental condition.

Table 3 shows the composition of residual elements in the ash. It is noted that the composition of each ash is calculated that 7 elements total is 100%. Regardless of heat-treatments, the residual elements in heat-treated ashes are almost same as those ashes, which means that all ashes are almost same characteristics to synthesize functional materials. These results suggested that heat-treatment is effective for the reduction of harmful substances elution, and Ash-4 via two-step heating is the best for elution inhibition and remaining the elements as raw material to synthesize functional materials. It is noted that weight reduction of the ash by treatment are 62.7% (Ash-1), 60.0% (Ash-2), 36.4% (Ash-3) and 26.2% (Ash-4), respectively, which means that waste reduction can be done by these treatment by burning carbonaceous contents and vaporizing metal oxide contents in the ash.

3.2 Products from raw ash and treated ash

Figure 5 and Table 1 show XRD patterns and chemical compositions of the products synthesized from (a) raw ash and (b) Ash-4, respectively. In the products from both ashes, tobermorite 11 Å [Ca₅Si₆O₁₅(OH)₂·5H₂O] and hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂] appeared, and both products have almost same chemical compositions, except ZnO and PbO. Tobermorite is the most

important compound in various hydrous calcium silicates and can act as a cation exchanger for NH₄⁺, Cs⁺, Sr²⁺ and so on [23, 24]. Hydroxyapatite is inorganic ion exchanger for both cation, Pb²⁺, Cd²⁺, etc., and anion, F⁻, etc. [25]. These are indicated that functional material with low harmful elements can be synthesized from the ash via heat-treatment.

4 CONCLUSION

A new two-step process, heating-treatment to separate harmful substances, such as Na, K, Cl, Zn and Pb, from the ash, and chemical conversion from the ash into functional materials with sodium hydroxide, was attempted. In heating-treatment, elution of Na⁺, K⁺ and Cl⁻ decrease using both air-heating and N₂-heating, those of Zn²⁺ and Pb²⁺ can be reduced by N₂-heating with PVC, but that of Cu²⁺ are unchanged by all heating-treatment. Mineral phases in heat-treated ash are mainly gehlenite, and the product from heat-treated ash via alkali reaction with 2 M NaOH solution at 180°C for 20 h contains tobermorite 11 Å and hydroxyapatite, and lower harmful substances, ZnO and PbO, than raw ash. Further research to optimize the treatment conditions, assess the heavy metal recovery and effect an appraisal of the potential of the material in wastewater treatment application is warranted.

Acknowledgment — “This work was supported by the Sumitomo Foundation.”

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Figure 5 XRD patterns of the product from (a) raw ash and (b) Ash-4.

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